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Novel Anionic Oligomerization by a New, Sequential Generation of Organolithium Compounds

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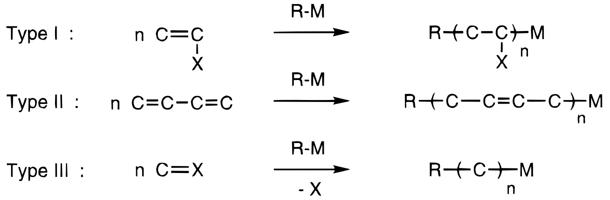
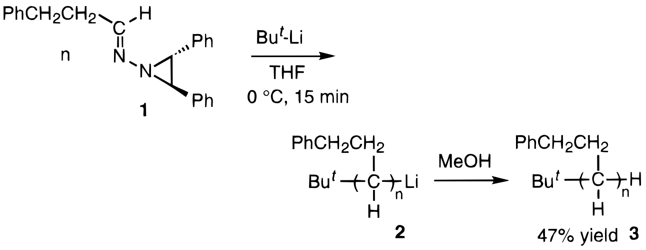
Anionic polymerizations (oligomerizations) are mainly divided into two classes depending on how the organometallic initiator is added to the monomeric substrates.[1] Most reactions are achieved with two-carbon propagations (type I in Scheme 1) which involve the sequential addition of carbanions to styrenes and α,*β*-unsaturated carbonyl compounds (e.g., methacrylates, vinyl ketones, etc.). The second type of the reaction (type II) involves the multiple 1,4-addition of carbanions to conjugate dienes, giving polymers (oligomers) with four-carbon elongations. Yet unknown is the one-carbon propagation in the anionic polymerization (oligomerization), which is categorized into the third, hitherto unexplored class (type III) of anionic polymerization (oligomerization). We report here the first example of this new type of anionic oligomerization.

Scheme 1

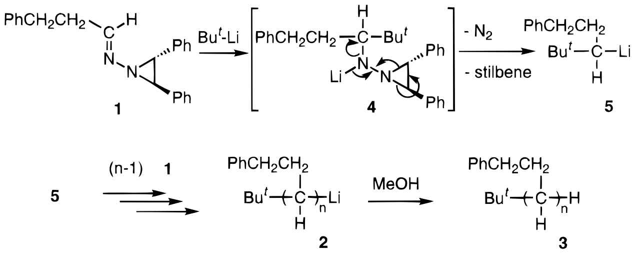


The anionic oligomerization of arylaziridine hydrazones of aldehydes can be effected under the influence of catalytic amounts of organolithium compounds to give oligo(alkylidene)s. As an example, hydrocinnamaldehyde *trans*-1-amino-2,3-diphenylaziridine hydrazone **1**[2] was treated with a catalytic amount (5 mol %) of *t*-BuLi in THF at 0 °C for 15 min to give, after quenching with excess MeOH, the hydrocarbon oligomer oligo(phenylpropylidene) **3** at a yield of 47%.[3] The ratio of the average molecular weight to the average number of molecular weights [M_w (=2139)/M_n(=1786)], as estimated from GPC using polystyrene as a standard, was 1.20. ^{1}H-NMR, ^{13}C-NMR, and IR spectra and elemental analysis indicated that the desired oligo(phenylpropylidene)s were produced,[4] while no other units were observed in the oligomers. When the oligomerization temperature was lowered to −20 °C under otherwise similar reaction conditions, the produced oligo(phenylpropylidene) **3** showed $M_{n,GPC}$ = 1382 with M_w/M_n = 1.35. Use of toluene in place of THF gave similar results. Changing the amount of *t*-BuLi initiator to 10 and 2.5 mol % gave oligo(phenylpropylidene) **3** with $M_{n,GPC}$ = 1215 (M_w/M_n = 1.43) and $M_{n,GPC}$ = 2496 (M_w/M_n = 1.18),[5] respectively. Similarly, BuLi and PhLi were equally effective as organometallic initiators: BuLi (5 mol %) 43% yield, M_n = 1673, M_w/M_n = 1.20; PhLi (5 mol %) 67% yield, M_n = 1506, M_w/M_n = 1.33. All of the oligo(alkylidene)s were very soluble in common organic solvents.



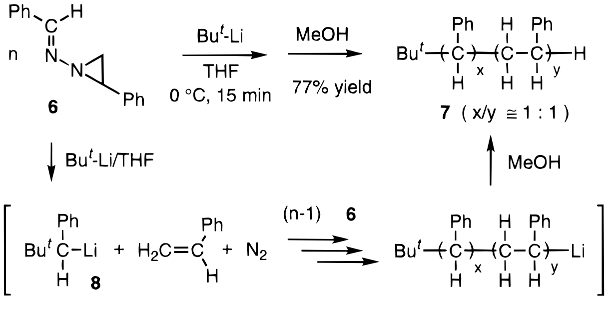
This reaction, as shown in Scheme 2, can be explained by the initial attack by *t*-BuLi on hydrazone **1** to give adduct **4**, which undergoes Shapiro-type fragmentation to furnish a new organolithium compound **5**.[6] Further sequential addition of the newly generated **5** and its higher homologs to the remaining, excess hydrazone **1** yields a carbon chain-elongated organolithium compound **2**. Quenching of **2** with MeOH gives the hydrocarbon oligomer **3**.

Scheme 2



It should be noted that use of the *trans*-2,3-diphenylaziridine moiety is crucial for the present anionic oligomerization to effect facile anionic fragmentation and subsequent carbon-chain extension. In the case of benzaldehyde 1-amino-2-phenylaziridine hydrazone **6**, cooligomerization of *in situ*-generated benzyllithiums (*e.g.*, **8**) with *in situ*-generated styrene occurred in THF solvent to give random cooligomer **7** (77% yield; M_n = 4717; M_w/M_n = 1.14 with 10 mol % of *t*-BuLi. Anal. Calcd for $(C_xH_y)_n$: C, 92.69; H, 7.31. Found: C, 92.37; H, 7.63) under similar oligomerization conditions.[7]

Scheme 3



In contrast to *trans*-1-amino-2,3-diphenylaziridine hydrazone **1**, a profound solvent effect was observed in the oligomerization of monomer **6**. Switching the solvent from THF to nonpolar toluene resulted in the predominant formation of azo-containing oligomer **9** (43% yield; M_n = 4786; M_w/M_n = 1.25 with 10 mol % of

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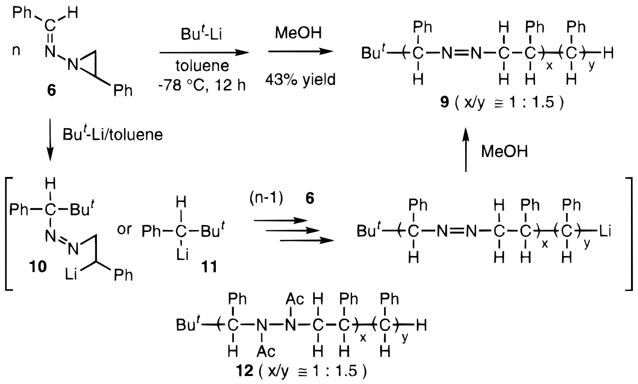
t-BuLi. Anal. Calcd for $(C_xH_yN_z)_n$: C, 81.05; H, 6.35; N, 12.60. Found: C, 85.02; H, 6.45; N, 7.53) from benzaldehyde 1-amino-2-phenylaziridine hydrazone **6** *via* organolithium intermediates of type **10** in preference to **11**. The existence of the azo functionality was characterized by Raman analysis (1537 cm^{-1} (N═N))[8] and further confirmed by transformation to **12** by reduction with $LiAlH_4$ followed by acetylation.

Scheme 4



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References and Notes

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(2) Muller, R. K.; Joos, R.; Felix, D.; Schreiber, J.; Wintner, C.; Eschenmoser, A. *Organic Synthesis*; Wiley: New York, 1988; Collect. Vol. VI, p 56.

(3) Buckley, G. D.; Cross, L. H.; Ray, N. H. *J. Chem. Soc.* **1950**, 2714.

(4) ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.36−7.64 (Ph−H), 0.47−3.05 ($2CH_2$, CH, and Bu^t); ^{13}C NMR (75 MHz, C_6D_6 at 70 °C) δ 143.7 (*ipso*-C), 127.6−130.0 (*ortho*-C, *meta*-C), 126.5 (*para*-C), 28.0−51.5 (2CH, CH, and Bu^t); IR (KBr) 3025, 2932, 1603, 1495, 1453, 1075, 1030, 907, 749, 698 cm^{-1}. Anal. Calcd for $(C_9H_{10})_n$: C, 91.47; H, 8.53. Found: C, 91.68; H, 8.32.

(5) The absolute M_n value was estimated from ^{1}H NMR measurement of ^{t}Bu group to be 2540 ($M_{n,theory} = 5967$).

(6) Vedejs, E.; Stolle, W. T. *Tetrahedron Lett.* **1977**, 135.

(7) Cooligomerization of hydrazone **6** with *in situ*-generated styrene proceeds with extrusion of nitrogen gas and small amount of *trans*-stilbene resulting from elimination of sequential benzylidene units.

(8) Harada, A.; Fujii, H.; Kamachi, M. *Macromolecules* **1991**, *24*, 5504.

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